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### (54) MANUFACTURE OF NBR-METAL COMPOSITE MATERIAL

(57)Abstract:

**PROBLEM TO BE SOLVED:** To effectively apply a post-vulcanization adhering method even by using an NBR containing an intermediate nitrile amount to a high nitrile amounts by post-vulcanizing the NBR in the state that an interface between an adhesive-treated metal and a white carbon-containing NBR vulcanized material is coated with a plasticizer having a specific value of a solubility parameter.

**SOLUTION:** As a metal for forming a composite material of an NBR coating, a stainless steel sheet or the like roughed on its surface by shot blasting or the like is used. As an NBR vulcanized material, a material surface-cleaned to remove a contaminant in a blooming brought about by a mold release agent, a plasticizer, a vulcanizer or the like is used. In a post-vulcanization adhering method using the NBR vulcanized material, an interface between an adhesive treated metal and the NBR vulcanized material containing a white carbon such as an anhydrous silica or the like is coated with a plasticizer such as a tricresyl phosphate or the like having a solubility parameter of 9.5 or above as an engaging liquid, the both are superposed, compressed, heated and post-vulcanized. Thus, this can be effectively applied even to the post-vulcanization adhering method of the NBR containing a low nitrile content to intermediate and high nitrile contents.

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CLAIMS

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[Claim(s)]

[Claim 1] The manufacturing method of the NBR-metal complex characterized by carrying out after cure after SP value has applied 9.5 or more plasticizers to the interface of the metal and white carbon content NBR vulcanizate which carried out adhesives processing.

[Claim 2] The manufacturing method of the NBR-metal complex according to claim 1 with which white carbon is used together with carbon black.

[Claim 3] an inside nitril content thru/or the crown -- the manufacturing method of the NBR-metal complex according to claim 1 or 2 with which NBR of a nitril content is used.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of NBR-metal complex. furthermore -- detailed -- an inside nitril content thru/or the crown -- also when NBR of a nitril content is used, it is related with the manufacturing method of the NBR-metal complex which can be applied effectively.

[0002]

[Description of the Prior Art] The approach of after-cure pasting-up method Post-Vulcanization Bonding Method is learned as an approach for making a metal and rubber vulcanizate paste up effectively. Although carried out in the vulcanization cycle of the rubber composition of the conventional pasting-up method inserting in superposition the metal and unvulcanized rubber by which adhesives processing was carried out, inserting these into metal mold, and heating, putting a pressure By this after-cure pasting-up method, carrying out heating vulcanization of the metal which carried out adhesives processing, and the rubber vulcanizate in metal mold is performed, and since rubber vulcanizate is vulcanized in metal mold as usual and vulcanization adhesion is carried out by subsequent actuation, the big merit on cost, such as metal mold being small and ending, is obtained.

[0003] As vulcanized rubber to which the after-cure pasting-up method is applied, synthetic rubber and natural rubber, such as SBR, chloroprene rubber, isobutylene isoprene rubber, and EPDM, are known, and load Far East company product KEMUROKKU 252 (1 acidity or alkalinity) and 234B etc. is used for the metal as adhesives by which application processing is carried out. And when the rubber vulcanizate to metal components needs to be pressed fit, it is supposed that process oil is effective as the fitting liquid.

[0004] however -- although it is comparatively satisfactory when such an after-cure pasting-up method is applied to NBR, and NBR is a low nitril content (17 - 25% of AN(s)) -- an inside nitril content (25 - 31% of AN(s)), and the crown -- in the case of the nitril content (31 - 36% of AN(s)), it became clear that \*\*\*\*\* after cure was not performed.

[0005]

[Problem(s) to be Solved by the Invention] the purpose of this invention -- an inside nitril content thru/or the crown -- also when NBR of a nitril content is used, the after-cure pasting-up method is to offer the manufacturing method of the NBR-metal complex applied effectively.

[0006]

[Means for Solving the Problem] After SP value has applied 9.5 or more plasticizers to the interface of the metal and white carbon content NBR vulcanizate which carried out adhesives processing, after cure of the purpose of this this invention is carried out, and it is attained by manufacturing NBR-metal complex.

[0007]

[Embodiment of the Invention] NBR covering is made and, generally a metal plate, for example, the stainless steel plate in which the front face carried out surface roughening by shot blasting, Scotch

whisky blasting, the hairline, dull finish, etc., a SPCC steel plate, an aluminum plate, an aluminium alloy plate, etc. are used as a metal which forms complex, and it is used after carrying out alkaline degreasing of it still more preferably. And using the adhesives like the above-mentioned, by dip coating, the spray method, brush painting, the rolling method, etc., spreading processing (about 10-50 micrometers of thickness) is carried out, and the front face is used.

[0008] On the other hand, as for NBR vulcanizate, it is desirable to use, after carrying out surface washing for removing the contamination by the blooming caused by a release agent, a plasticizer, the vulcanizing agent, etc., and surface washing is performed by approaches, such as vapor degreasing by the chlorine-based solvent, a tumbling by alkali cleaning, and ultrasonic cleaning.

[0009] Although carbon black is blended as a reinforcing agent and a bulking agent and it is generally used into rubber if it is in the case of NBR -- as the thing and angle of a low nitril content -- an inside nitril content thru/or the crown, although after cure did not carry out \*\*\*\*\* advance and the after-cure pasting-up method was not able to be applied, if it was in the thing of a nitril content After-cure adhesion is made to enable there more than the about 5 weight section per NBR100 weight section by blending the white carbon of the about ten to 100 weight section preferably.

[0010] As white carbon, an anhydrous silica, a water silica, a calcium silicate, etc. are used, and, generally this is preferably used together with the carbon black used at a rate of the about ten to 100 weight section more than the about 5 weight section per NBR100 weight section.

[0011] By the after-cure pasting-up method using NBR vulcanizate, white carbon is blended there, a request is inadequate, and as fitting liquid of that, 9.5 or more, preferably, SP value (solubility parameter) is used, after the plasticizer of 9.5-10.2, for example, tricresyl phosphate, dibutyl phthalate, etc. have applied the plasticizer to the interface of the metal and white carbon content NBR vulcanizate which carried out adhesives processing. the case where the process oil known from the former when SP value uses the plasticizer not more than this is used -- \*\*\*\*\* -- or after cure is not performed at all.

[0012] In order to secure the close contact between the metals and white carbon content NBR vulcanizate which were piled up and which carried out adhesives processing, about 5 to 35%, what applied the plasticizer to both interface in such the condition is in the condition generally compressed about about 5 to 10%, using heating apparatus, such as oven and an autoclave, is heated an about 10-minute room thru/or about 2 hours of abbreviation at about 140-180 degrees C, and performs after cure.

[0013]

[Effect of the Invention] this invention approach -- not only a low nitril content but an inside nitril content, or the crown -- it is applied effective also in the after-cure pasting-up method of NBR of a nitril content, and manufacture of NBR-metal complex, such as a rubber vibration insulator and various industrial use articles, is enabled.

[0014]

[Example] Next, this invention is explained about an example.

[0015]

Examples 1-2, the examples 1-19 of a comparison NBR The 100 weight sections FEF carbon black (CB) (Specified quantity) A water silica (Specified quantity) Dioctyl phthalate Six weight sections A zinc oxide 5 \*\* Stearic acid 1 \*\* An antioxidant (IPPD, TMDQ, etc.) 5 \*\* sulfur 1 \*\* vulcanization accelerator After kneading each combination component more than 4 \*\* with a kneader, press cure was carried out for 10 minutes at 180 degrees C, and the vulcanized-rubber test piece (6.4mm in the object for JIS bend tests, thickness) was produced.

[0016] On the SPCC steel plate test piece (1.5mm in thickness) front face which processed [ shot-blasting-] and processed [ cleaning-] After carrying out the spray coating cloth of the commercial adhesives for solvent mold NBR (KEMUROKKU 252) (about 15 micrometers of thickness), Various kinds of following oil TCP:tricresyl phosphate (SP9.7) DOP:dioctyl phthalate (SP9.0) DOS:dioctyl sebacate (SP8.4) process oil : A naphthene (SP8.2) is applied with the brush. The above-mentioned press cure rubber test piece was attached there in piles to the compression fixture, and where the rubber section is compressed 10%, after cure of 1 hour was performed at 150 degrees C.

[0017] Air cooling was carried out, and when the JIS K-6301 90" friction test was performed and it

asked for the rubber section residual percentage of an adhesives spreading side about the NBR-metal complex wide opened from the fixture, the result as shown in the next table was obtained.

A table Spreading oil Rubber Example NBR CB (section) SiO<sub>2</sub> (section) TCP DOP DOS Naphthene Remaining rate (%) example 1 Inside nitril 50 15 O 100 \*\* 2 nitril \*\* the crown -- \*\* O Example 1 of 100 comparisons Low nitril 65 90 \*\* 2 inside nitril [ \*\* ] -- 5 \*\* 3 nitril \*\* the crown -- 0 \*\* 4 Inside nitril 50 15 65 \*\* 5 nitril \*\* the crown -- \*\* The nitril 65 in 50 \*\* 6 O 6 \*\* 7 nitril \*\* the crown -- O 2 \*\* 8 Inside nitril \*\* O 0 \*\* 9 nitril \*\* the crown -- O 0 \*\* 10 Inside nitril 50 15 O 12 \*\* 11 nitril \*\* the crown -- \*\* O 10 \*\* 12 Inside nitril 65 O 0 \*\* 13 nitril \*\* O the crown -- 0 \*\* 14 Inside nitril 50 15 O 9 \*\* 15 nitril \*\*\*\* the crown -- O 7 \*\* 16 Inside nitril 65 O 0 \*\* 17 nitril \*\* O the crown -- 0 \*\* 18 Inside nitril 50 15 O the 3 \*\* 19 crown -- nitril \*\*\*\* O 1 Nitril NBR:AN 28% in notes low nitril NBR:AN 18% the crown -- nitril NBR:AN 33.5% [0018] The following can say from the above result.

(1) Although an adhesive property can improve when \*\*\*\*\* after cure is not carried out in the carbon black compound of NBR more than inside nitril although the good adhesive property was acquired in the case of the low nitril NBR when oil was not applied to the interface of the metal and NBR press cure rubber which carried out adhesives processing, as shown in the examples 1-5 of a comparison, but a water silica is used, it is still inadequate.

(2) the case (examples 16-19 of a comparison) where the process oil known from the former as spreading oil when SP value uses less than 9.5 oil (examples 8-15 of a comparison) is used -- \*\*\*\*\* -- or don't carry out after cure at all.

(3) When SP value uses 9.5 or more oil and only carbon black is used (examples 6-7 of a comparison), don't carry out \*\*\*\*\* after cure.

(4) On the other hand, after-cure adhesion which becomes enough can be performed in this invention (examples 1-2).

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